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THE UNIVERSITY OF ALBERTA

THE MERCURY PHOTSENSITIZED DECOMPOSITION  
OF CYCLOPENTENE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL  
FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER  
OF SCIENCE IN CHEMISTRY

DEPARTMENT OF CHEMISTRY

BY

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To my wife



## Abstract

The mercury photosensitized decomposition of cyclopentene has been studied at room temperature as a function of cyclopentene pressure in the range 20 to 140 mm, and as a function of exposure time from 2.5 to 30 minutes at a pressure of 82 mm. The major products have been shown to be vinyl cyclopropane, cyclopentyl cyclopentene, cyclopentenyl cyclopentene, bicyclopentyl and hydrogen in decreasing order of importance. Trace quantities of cyclopentane, cyclopentadiene and 1:4 pentadiene were also formed. Polymer appeared particularly at low pressures.

The definite suppression of the decomposition with increasing substrate pressures, the action of nitric oxide and the comparison with work on other olefins leads to the conclusion that all products arise from the same electronically excited state of cyclopentene. Vinyl cyclopropane is formed by direct isomerization and the  $C_{10}$  hydrocarbons by radical addition to the substrate and radical recombination reactions. A mechanism is proposed to fit the data.



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## Introduction

Photochemistry, arbitrarily defined, is that branch of chemistry concerned with the action of visible and ultra violet light on matter. With these forms of radiant energy it is possible to raise most atoms and molecules to an electronically excited state. The relative values of the electronic energy levels within the recipient atom or molecule determine the wave length of the light to be used. On absorbing, molecules containing only light atoms (e.g. hydrocarbons) are raised to an electronically excited state. Only those transitions are allowed in which the excited state is of the same multiplicity as the ground state.

After initial excitation the excited species may lose its energy in any of the five following ways:

- (1) Fluorescence; radiative conversion to the ground state.
  - (2) Internal conversion; non-radiative conversion to the ground state.
  - (3) Intersystem crossing; non-radiative transition which involves spin intercombination to the triplet state.
  - (4) Photochemical reaction; by unimolecular dissociation or intermolecular reaction; and
  - (5) Energy transfer; non-radiatively to a neighbouring molecule.
- The yield of photochemical products depends on the rate of (4) compared with the others. Products may also be obtained via the triplet state formed by (3) - or a triplet state formed in the initial excitation step. As well as photodissociation



the triplet state can lose its energy by phosphorescence, internal conversion and triplet-triplet energy transfer to another molecule.

To raise a molecule to an excited state it must be supplied with energy. There is no problem if the molecule absorbs in a convenient region of the spectrum ( $>2200^{\circ}\text{A}$ ). The photolysis of acetone and anthracene are common examples of this. In the case of molecules, like the hydrocarbons, which do not absorb at suitable wavelengths, a sensitizing agent must be added which will absorb light and transfer its energy of excitation through collisions.

There are many reasons why mercury has found such wide use as a photosensitizer in the gas phase. Principally these are as follows:

- (1) the spectroscopy of the mercury atom has been extensively studied. It is known to have a large absorption coefficient for radiations at  $1849^{\circ}\text{A}$  and  $2537^{\circ}\text{A}$ .
- (2) it has a high vapour pressure at room temperature where most molecules are stable.
- (3) Good, monochromatic light sources are available; and
- (4) it is usually chemically inert to both substrate and products.

The low pressure mercury arc with suitable filters is an excellent source of  $2537^{\circ}\text{A}$ . radiation. The mercury atom in its ground state,  $6(1\text{S}_0)$ , can absorb this and go



to the  $6(^3P_1)$  state. The triplet state has been found experimentally to have a lifetime of approximately  $10^{-7}$  sec., from which, if left undisturbed, it will normally undergo radiative conversion to the ground state. This emission is known as resonance radiation.

When mercury vapour is irradiated in the presence of a foreign gas, the excited atom may lose its energy by collision before it can fluoresce. The extent to which the fluorescence is quenched depends on the pressure of the gas and the efficiency of the collisions between the excited atom and the substrate. The quenching cross-section of a molecule is a measure of its quenching efficiency. Paraffins show a large increase in quenching cross-section with molecular weight, ranging from  $0.085 \times 10^{-16} \text{ cm}^2$  for methane to  $29 \times 10^{-16} \text{ cm}^2$  for n-heptane. Olefins have a larger quenching cross-section than the corresponding paraffins but the change with molecular weight is not so marked. For ethylene it is  $48 \times 10^{-16} \text{ cm}^2$  and benzene has the largest value,  $59 \times 10^{-16} \text{ cm}^2$ . Cyclopentene has not been measured but from comparison with other olefins  $54 \times 10^{-16} \text{ cm}^2$  is a reasonable approximation.<sup>1</sup>

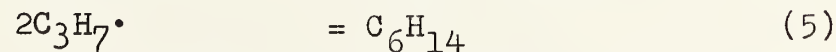
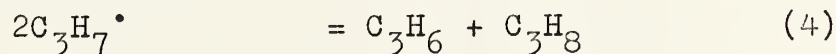
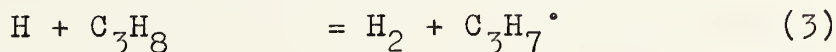
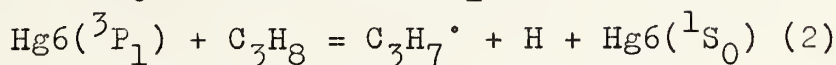
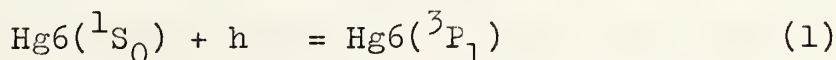
The two main quenching processes in hydrocarbons involve formation of an excited molecule and dissociation. The normal state of hydrocarbons is a singlet state. From spin conservation considerations an excited molecule, if formed in the quenching process, must be in the triplet state.



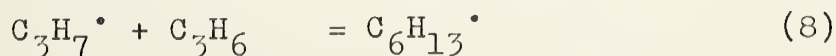
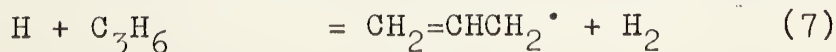
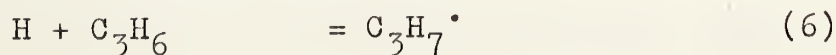
Unless a hydrocarbon molecule has a low lying triplet state it should dissociate on colliding with the triplet mercury atom. Steacie has summarized this.<sup>1</sup>

Experimentally, all the alkanes have been shown to decompose by an initial C-H bond scission. If an excited molecule is formed at all in these reactions its lifetime must be exceedingly short compared with the time between collisions. An excellent review of the question of intermediate HgH formation is available.<sup>1</sup>

The saturated hydrocarbons have been extensively studied. Since there seems to be little discrepancy in the results only propane will be discussed as an example. At high propane pressures, low light intensity and low extent of decomposition the overall mechanism can be represented by 2,3.

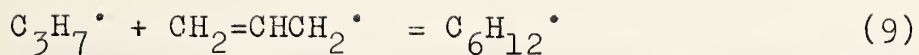


The  $\text{C}_3\text{H}_7^\bullet$  radical can be the normal or isopropyl radical. As propene collects in the system the following additional reactions may become important.









Since propane is finding use as an actinometer in mercury photosensitizations it seems pertinent to mention more about the reaction. The propylene is formed by (4), accumulates in the system and acts as a scavenger for hydrogen atoms generated in the primary process. As the extent of propane decomposition increases a steady state is attained in which the rate of formation of propylene by disproportionation of propyl radicals equals the rate at which it is consumed by (6) and (7). It is assumed for the purposes of actinometry that the quantum yield of hydrogen production at the steady state is 0.5.

The literature of the last five years has shown increasing interest in the field of energy transfer. Within this general framework mercury photosensitization is being shown more attention. Papers have appeared on ethylene, propylene, the butenes and pentenes. There seems to be little doubt that the initial process is formation of an excited molecule. The evidence for this is that in all molecules studied, there is a decrease in the extent of decomposition with increasing substrate pressure. Where inert gases have been added they have been found to have a similar effect.

Although it is generally accepted that an excited



molecule is formed in the primary process there still remains the question of its nature and subsequent fate. Since the most important contributions to this aspect of mercury photosensitized olefin decompositions have been made on ethylene and butene-2 these will be reviewed in some detail.

Two decomposition processes for the excited ethylene molecule have been found. Hydrogen and acetylene are formed by an intramolecular process. Confirmation of this was obtained by Callear and Cvetanovic<sup>5</sup> who found only  $H_2$  and  $D_2$  from a mixture of  $C_2H_4$  and  $C_2D_4$ . The free radical mode of decomposition forms vinyl radicals and hydrogen atoms. Robb and coworkers<sup>15</sup> have studied this aspect of the reaction. Lossing, Marsden and Farmer<sup>6</sup>, using a reactor coupled to a mass spectrometer found that at room temperature only three percent of the ethylene decomposes to form free radicals.

Further deuteration studies of Cvetanovic and Callear<sup>5</sup> have shed some light on the nature of the excited ethylene molecule. Cis dideuteroethylene gave, after illumination, not only the expected trans form but ethylene-1,1- $d_2$ . The appearance of the latter in the products suggests that at some stage in the life of the excited molecule, the hydrogen and deuterium atoms become delocalized. Alternatively,



formation of an excited ethylidene biradical has been proposed.

At higher temperatures and low pressures the free radical decomposition of ethylene becomes more important,<sup>7</sup>

eventually masking the molecular decomposition.

Addition of nitric oxide was found to restore the conditions of product formation prevalent at room temperature. Porter<sup>8</sup> has proposed that this evidence might be explained by two different excited molecules each decomposing in its own way. This question still remains unanswered.

Butene-2 seems to fit the general pattern of olefin decompositions. The pressure dependence of the decomposition has been clearly shown first by Gunning and Steacie<sup>9</sup> and later by Cundall and Palmer<sup>10</sup>. The existence of cis and trans isomers of butene-2 has added interest to the study of this reaction. Gunning, Cvetanovic, and Steacie<sup>11</sup> found that cis-trans isomerization at 60 mm pressure occurred readily. Isobutene and butene-1 under the same conditions showed little isomerization. They explained their results with butene-2 by the uncoupling of the  $\pi$  electrons forming a vibrationally excited triplet state molecule which undergoes collisional isomerization to either cis or trans butene-2. The nature of the butene-1 or isobutene molecule makes detection of a similar reaction





impossible. Other isomerizations occurred only to a small extent in all the butenes.

Cundall and Palmer<sup>10</sup> observed the effect of substrate pressure on the mercury photosensitized decomposition of butene-2. Percentage decompositions were small in all cases and the amounts of products other than the butene-2 isomer were also small except at pressures lower than 30 mm. Side products decreased on adding gases. Radical sources such as acetone, diethyl mercury and hydrogen decreased the rate of cis-trans isomerization. Except at very long exposures the yields of  $C_8$  products were considerably smaller than either of the cis-trans isomers.

To prove that the triplet mercury atom is not unique in producing cis from trans butene-2, Cundall and Palmer used sulphur dioxide and biacetyl as photosensitizers with butene-2. The wave length of the irradiating light was chosen in each case so that sulphur dioxide and biacetyl were produced in their triplet state, the energies of which are 73 and 56 K cal respectively. Both were found to bring about cis-trans isomerization.

All the above observations led them<sup>10</sup> to suggest the existence of two excited triplet state molecules. Cis-trans isomerization occurred from the ground triplet state and free radical and other rearrangement products arise





from the vibrationally excited triplet.

The mercury photosensitized decomposition of butene-2 has been studied by mass spectrometry<sup>6</sup>. The only products detected were butadiene, hydrogen and propylene, all of which can be accounted for by scission of a  $\beta$  C-H bond forming a resonance stabilized methallyl radical. This radical can undergo photosensitized decomposition or dimerize. Neither cis-trans or other isomeric butenes were found in the products. Avrahami and Kebarle<sup>13</sup> by varying the pressure of helium carrier gas from 10 to 100 mm in a mass spectrometric study showed that even here an excited molecule is formed. At low helium pressures there was evidence for both cis trans isomerization and bond rupture. The bond rupture reaction decreased at high pressures by a factor of two while the isomerization increased correspondingly. The propylene and isobutene (6,9,10) molecules are similar to butene-2 and have been found to follow the same pattern as butene-2. An excited molecule which decomposes to products by breaking a C-H bond.

A paper by Majer, Mile and Robb<sup>14</sup> in which the isomerization of butene-1, 2-methyl butene-1, pentene-1 and pentene-2 are studied at low pressures and high extents of decomposition has just been published. They found butene-2 to be major product in the butene-1 reaction whereas other workers<sup>10,11</sup> did not detect it in any appreciable amounts. Similarly 2-methyl butene-1 gave



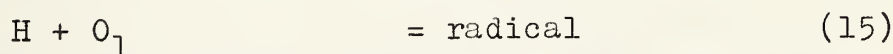
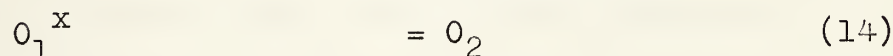
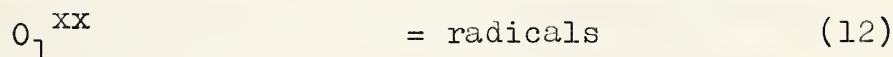
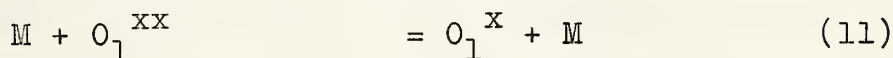
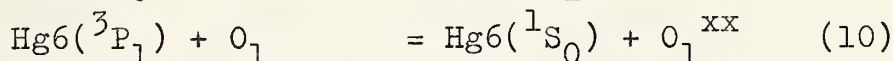
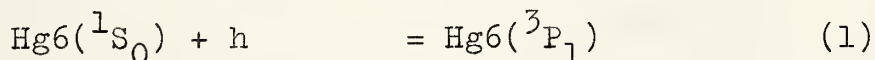
the rearrangement products 2-methyl butene-2 and 3-methyl butene-1. The formation of isopentane in relatively large amounts indicated that these isomers are formed by hydrogen atom addition to the substrate to give an isopentyl radical which rearranges before disproportionation or elimination of the hydrogen atom. Robb does not make his ideas clear on this point, nor did he study the recombination products in the reactions.

The decomposition of olefins photosensitized by mercury is a field in which the experimental evidence leaves room for large differences of opinion concerning the mechanism. According to the Wigner-Witmer correlation rule<sup>15</sup> transfer of energy from mercury atoms in the  $6(3P_1)$  state to olefins should occur comparatively readily. The experimental fact that triplet mercury atoms do not remove hydrogen atoms from the olefins, as they do from paraffins, leads to the conclusion that interaction is between the metal atom and the  $\pi$  electrons. The ground triplet state of olefins should not be more than 50 kcal above the ground state. Transfer of 112 kcal from the triplet mercury atom should therefore leave the olefin with about 70 kcal of vibrational energy<sup>17</sup>. The suppression of decomposition with pressure and added inert gases confirms this. However, where information is available cis-trans isomerization reactions are relatively more important at high pressures and vice-versa. This, and the work of Cundall and of Kebarle point to isomerization taking place after removal of the vibrational energy by collision. Also,



isomerization by rearrangement seems to be explainable only, as described by Robb for 2-methyl butene-2, by a free radical process. It appears feasible to assume that it is the vibrationally excited molecule which decomposes to free radicals. The temperature effect on the ethylene reaction is further evidence for this process.

A general mechanism which might account for the high, the low pressure and mass spectrometric studies on the mercury photosensitized decompositions of olefins is as follows:

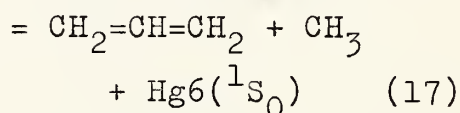
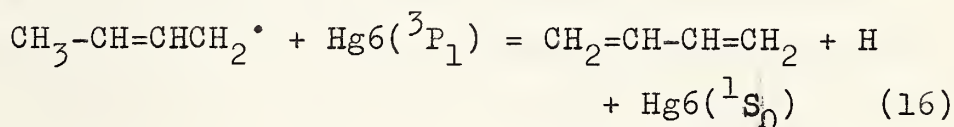


Here  $\text{O}_1^{\text{xx}}$  is the olefin molecule in the vibrationally excited triplet state;  $\text{O}_1^{\text{x}}$  represents the olefin in the ground triplet state. Reaction (11) can account for the pressure dependence of the decomposition. The isomerization from the ground triplet state olefin by (14) is competing with the free radical decomposition from the excited triplet molecule by reactions (12) and (13). The radicals formed





in these latter reactions are of the resonance stabilized allyl type. It is assumed they can dimerize, abstract or disproportionate at normal pressures. In the mass spectrometer, the low pressures of olefin and relatively high pressure of mercury makes their mercury photosensitized decomposition become important. The methallyl radical from butene-2 can thus react as follows:



The formation of polymer has been noticed in all olefin reactions. An explanation can be found in a chain reaction in which the radicals add to the substrate forming a radical dimer which can dimerize disproportionate or add to give a radical trimer, etc. Since decomposition into radicals increases in importance at low pressures reaction (15) should also become important. This should be particularly true in the studies of Robb and coworkers who also went to large extent of decompositions.

In view of what has been said above it was felt that there are certain advantages in simplicity to be gained by studying cyclic olefins. Firstly cis-trans isomerization is not possible due to the geometry of the





double bond. Furthermore, if  $\beta$  C-C scission occurred only one fragment would form. Of itself, the study of such a fragment would be interesting since it would be at the one time, a biradical and an allylic radical. Breakage of the  ~~$\beta$~~  $\beta$  C-H bond would yield a cyclic allyl radical plus a hydrogen which should be efficiently scavenged by the substrate to yield a stable saturated cyclic radical, the behaviour of which have been worked out<sup>19</sup>.



## EXPERIMENTAL

1. Materials

Phillips Research grade cyclopentene with a stated purity of 99.72% was used in all runs except those marked with an asterisk (Table IIA and IIIA). Gas chromatographic analysis on silica gel showed the impurity level, after degassing, distilling from liquid nitrogen into a trap cooled in dry-ice-acetone backed by the pump, to be 0.2 mole percent. Of this 0.15% was cyclopentane, the rest was cyclopentadiene.

The cyclopentene used in runs marked with an asterisk inadvertently showed 3% cyclopentane impurity. Since it had been shown that cyclopentane was not a product of any importance this cyclopentene was not further purified. Comparison of the quenching cross-sections and radical scavenging abilities of cyclopentane and cyclopentene leads to the conclusion that it would not affect the results. This was borne out in practice.

The nitric oxide used was taken from a cylinder of Matheson's C. P. grade nitric oxide. Impurities were removed by twice distilling from liquid oxygen taking the middle fraction each time.

Matheson "Instrument Grade" propane was used in the actinometric runs. Its stated purity was 99.9%. It was purified before use by trap to trap distillation, the middle fraction being retained.

Bicyclopentyl was prepared by Stock (19). Gas chromatographic analysis showed the presence of 4% of one other  $C_{10}$



hydrocarbons. It was used in calibration of the gas chromatograph without further purification.

## 2. Apparatus.

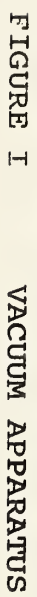
### (i) Low Vacuum System

The low vacuum system is not shown in any diagram. It was constructed of pyrex glass tubing, the main manifold being 12 mm O.D. and the connections to it 7 mm O.D. The system was evacuated with a Welch high-vacuum duoseal two stage mechanical pump. The purpose of the low vacuum system was to lower the mercury levels in the McLeod gauge, Toepler pump and the various mercury float valves. A ground glass stopcock connected the high and low-vac systems.

### (ii) High Vacuum system.

The system was evacuated using a two-stage high speed mercury diffusion pump backed by a Cenco Hyvac 7 two stage mechanical pump. The two were joined via a standard taper removable trap, a high vacuum stopcock and a length of rubber tubing. To prevent contamination of the pump oil the trap was kept permanently at liquid nitrogen temperatures. Provision was made for evacuating the system without using the mercury diffusion pump and for removing the trap for cleaning without disturbing the remainder of the system.





# VACUUM APPARATUS





The main manifold was constructed of 20 mm O.D. pyrex tubing. 12 mm O.D. tubing was used throughout the rest of the high vacuum system with the exception of the spiral trap which was made of 7 mm O.D. tubing.

Figure 1 is a schematic diagram of the apparatus. That part of the system which came into frequent contact with hydrocarbons was kept free of stopcocks. Grease-free mercury float valves  $H_1$  to  $H_6$  were used instead.  $H_5$  was modified in that only one side had a mercury float valve; the other side was continuous with the 2 mm capillary of the smallest volume on the gas buret. The latter was connected to the storage-reaction system at E and to the main manifold at E and G via stopcocks  $K_1$  and  $K_2$ . Situated between the Toepler pump and the reaction system were  $H_4$ , the spiral trap  $C_1$  and one stage mercury diffusion pump D. The McLeod gauge, L, was connected between D and the Toepler pump.

Twin reaction vessels  $R_1$  and  $R_2$  were attached to the remainder of the apparatus by standard tapers T and float valves  $H_2$  and  $H_3$ . Sealstick cement was used to connect the two parts of the standard tapers. A capillary manometer, M, and a small finger trap, P, 3" long and 9 mm diameter, were attached to each cell.



Reagents were introduced into the high vacuum system at A where they were degassed and purified using traps C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>. From here they could be transferred to any part of the system via the manifold.

Sampling bulbs for mass spectrometric samples were attached to the Toepler pump at stopcock K<sub>5</sub>.

(iii) Gas Liquid Chromatograph.

All analyses of condensible gases were performed on the Kromotog K-2 G.L.C. unit supplied by the Burrell Company. The columns were 2½ m long by 0.25 ins I.D. One column was packed with 25%  $\beta\beta'$  oxydipropionitrile. on 30-60 mesh firebrick, the other with Burrell Corporation Medium Activity Silica Gel #341-144. Helium carrier gas was used, for all analyses. With the silica gel column the flow was set at 120 ml/minute at the beginning of each analysis. This flow rate was measured with a soap bubble flow meter and was found to change drastically during temperature programming.

(iv) Light Source.

The low pressure mercury arc Hanovia No. 88A - 45 was housed in a simple metal box, two sides of which were covered with a Corning No. 7910 filter to ensure removal of 1849 Å<sup>o</sup> radiation. Two quartz cells were placed approximately 3½ inches from the lamp. A



fan circulated air at room temperature within the lamp housing.

(v) Other Instruments.

Instrumental analyses were performed on the Perkin-Elmer 221 G Infra red Spectrophotometer; the Varian A60 Nuclear Magnetic Resonance Spectrometer and the Metropolitan Vickers Mass Spectrometer, type MS2.

3. Operational Procedure.

Once the cyclopentene was in the storage vessel care was taken to ensure that it never again came into contact with any other gas, condensible or noncondensable. However to ensure that it was still pure at the beginning of each run, it was degassed twice inside the storage vessel. Only when the pressure in the whole system, with cyclopentene at liquid nitrogen temperature, fell to  $10^{-6}$  mm Hg was the cyclopentene allowed to expand into the reaction vessel. This was done by closing  $H_4$  and  $H_6$  and allowing the cyclopentene to vapourize until the manometer in each reaction vessel showed the desired pressure. The valve to each reaction vessel was then closed, the pressure read on the cell manometer and the cyclopentene left overnight to equilibrate with the mercury. The same procedure was used for blank runs.



The lamp with its cooling system was allowed to warm up for one hour before starting a run. Timing commenced with removal of the shutter between the lamp and cell and terminated with switching off the lamp. Immediately a run was complete the small finger trap on each reaction vessel was immersed in liquid nitrogen. At least two hours were allowed for all condensible products to condense into the finger trap.

With the latter still immersed in liquid nitrogen all products noncondensable at liquid nitrogen temperatures were pumped into the gas buret where their volume, pressure and temperature were taken. The Toepler pump and small mercury diffusion pump were used for pumping during this process. The spiral trap C, was immersed in liquid nitrogen to ensure that no condensible gases interfered with the measurement of the noncondensibles. By lowering H<sub>5</sub>, the latter could be expanded into a previously evacuated bulb for mass spectrometric analysis.

The small finger traps were sealed under vacuum and removed for subsequent analysis by gas chromatography. With the tip of the sample phial immersed in liquid nitrogen, it was scratched with a







file and broken open. Before the products had time to evaporate a rubber connection and silicone seal were placed over the opening. The products were removed by syringe and injected into the column of the gas - liquid chromatograph. The variac on the chromatography unit was set at 60 volts at the air peak and then to 90 volts at the emergence of the major C<sub>5</sub> product. Under these conditions cyclopentene emerged at 75°C and bicyclopentyl at 145°C.

To calibrate the chromatography unit a known mixture of cyclopentene and bicyclopentyl was run through under conditions of temperature programming identical with those used for product analysis. The calibration factor for the C<sub>10</sub> hydrocarbons (assuming a value of unity for the C<sub>5</sub>'s) was obtained by dividing the area ratio by the mole ratio. The assumption was made that all C<sub>5</sub> hydrocarbons have a calibration factor of unity and that the C<sub>10</sub> hydrocarbons have the same value as bicyclopentyl. These assumptions were made necessary by the lack of standard compounds.

##### 5. Actinometric Procedure.

The production of hydrogen in the mercury photosensitized decomposition of propane has been studied as a function of pressure, exposure time and light



intensity 2,3 . In this study the rate of hydrogen production at propane pressures of 300 mm was measured at intervals of time. It was found in agreement with Back<sup>3</sup> that the rate only became constant after approximately 1% decomposition. At this point of constant rate of hydrogen production the assumption was made that the quantum yield of hydrogen production equals 0.5 moles/einstein.

The procedure for introducing propane was identical to that described for cyclopentene. It was thoroughly degassed; expanded into both reaction vessels to a pressure of 305 mm; equilibrated for four hours; exposed to the previously warmed up light source for ten minutes; the products frozen down in liquid nitrogen; and the hydrogen pumped off and measured in the gas buret. The propane was again allowed to warm up, equilibrate inside the reaction vessel and the procedure repeated until the amount of hydrogen from a ten minute run remained constant.



## Results

## 1. Actinometry

The procedure and theory behind the actinometry have been discussed (Chapter II). The yield of hydrogen, from a ten minute run, in mm Hg, the gas buret volume being 8.027 ml, is tabulated for each cell in Table IA. Each reaction vessel had a volume of  $217 \pm 4$  ml.

Table IA

Time from start	H <sub>2</sub> yield in mm Hg, Vol = 8.027, Temp = 28°C.	
	Left Cell	Right Cell
10 min.	39.50 mm.	31.65 mm.
20	24.85	19.60
50	21.30	15.65
60	19.15	13.80
70	21.85	17.40

From these figures, the rate of hydrogen production in moles/minute was calculated and hence the light intensity for the left and right cell were  $3.94 \times 10^{-6}$  and  $2.96 \times 10^{-6}$  einsteins per minute respectively.

Twice throughout the study the lamp was changed and the light intensity redetermined as already described. Table IB shows these light intensities and the run number range in which they were used.

Table IB Light Intensities (Einsteins/min)

Left Cell		Right Cell	
Run No.	Light Intensity	Run No.	Light Intensity
39 to 51	$3.54 \times 10^{-6}$	40 to 52	$2.46 \times 10^{-6}$
53 to 79	$3.75 \times 10^{-6}$	54 to 80	$2.38 \times 10^{-6}$
79 on	$3.96 \times 10^{-6}$	82 to 128	$2.96 \times 10^{-6}$



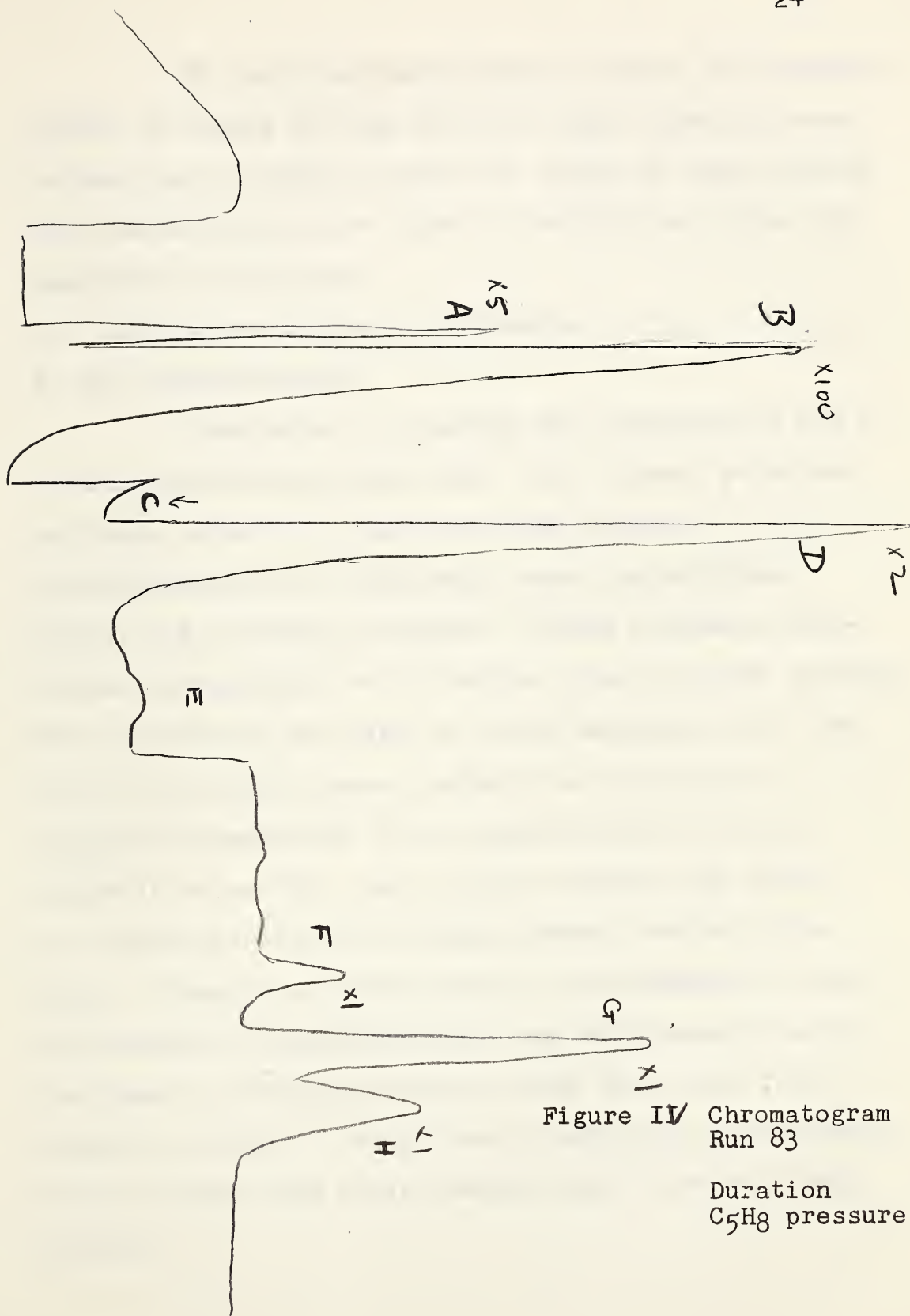


Figure IV Chromatogram  
Run 83

Duration = 15 min  
C<sub>5</sub>H<sub>8</sub> pressure = 80 mm





To facilitate conversion of moles into quantum yields in Tables IIA and IIIA the light intensity used in each run is shown in the last column of these tables. Even numbered runs were done in the left cell, the odd numbered in the right.

## 2. Qualitative Analysis of Products.

### a) Gas chromatography

Separation of products was attempted on 2.5 m columns containing silica gel, ucon, didecyl phthalate, silicone rubber 550, carbowax 1500, apiezon L,  $\beta$   $\beta'$  oxydipropionitrile, polyphenyl ether, polyethylene glycol and tricresyl phosphate. Where necessary temperature programming was attempted. Out of these columns that were tried the only one which separated both the  $C_5$  and  $C_{10}$  hydrocarbons products was silica gel. A typical chromatogram of the products from a run is shown in Figure IV. Two distinct regions can easily be discerned, one for  $C_5$  hydrocarbons, the other for  $C_{10}$ 's. Samples of cyclopentane, cyclopentene, 1:4 and 1:3 pentadiene, cyclopentadiene and bicyclopentyl were run under conditions identical with those used for a typical analysis. Comparison of retention times showed that of these only bicyclopentyl could be significant product.



25%  $\beta,\beta'$  oxydipropionitrile on firebrick gave excellent separations of all the  $C_5$  products. The  $C_{10}$  fraction did not elute from this column. Again only one major  $C_5$  component was found. Its retention time again did not coincide with any standard  $C_5$  compound that was available commercially.

Small amounts of cyclopentane, 1:4 pentadiene and cyclopentadiene were formed under all conditions and were found to increase in importance at lower pressures and long exposure times. On the propionitrile ether column, 1:4 pentadiene was eluted with cyclopentane.

Of all the more probable  $C_{10}$  products only bicyclopentyl was available for retention time comparison. Addition of bicyclopentyl to the reaction products gave enrichment of peak F (Figure II) relative to the other products.

Lutwick<sup>20</sup> found that a 7 cm tube containing 25% concentrated sulphuric acid on firebrick when placed between the injection system and the column, selectively removed alkenes, allowing only saturated hydrocarbons to pass through the column. Employing this technique, only peaks A and F were eluted from silica gel. This was repeated with a sample of reaction products to which bicyclopentyl had been added. Again only one  $C_{10}$  peak



was found.

From gas chromatographic studies it can therefore be concluded that all the products are unsaturated except two whose retention times correspond to cyclopentane and bicyclopentyl. A blank run with cyclopentene showed that only small amounts of cyclopentane were formed. The other  $C_5$  and  $C_{10}$  products must be unsaturated. The major  $C_5$  product was not a pentadiene.

b) Infra red spectroscopy.

A short resume of the information that can be deduced from hydrocarbon spectra will be given at this point<sup>18</sup>.

The absence of a band at  $1385 \pm 10 \text{ cm}^{-1}$  denotes there are no methyl groups present in a sample. This band is so intense it has been used for determining the number of C methyl groups in a molecule. The C=C absorption band is generally not very intense. If the double bond is conjugated, terminal or attached directly to a ring as with methylene cyclobutane, the intensity is considerably enhanced. The position of this band usually moves to around  $1610 \text{ cm}^{-1}$  if it is conjugated.

The C-H stretching frequency in the  $3100 - 2800 \text{ cm}^{-1}$  region has been used for determining to which type



of carbon atom the hydrogen is attached. The  $\text{C}=\text{CH}_2$  shows two bands, one at  $3095 - 3075 \text{ cm}^{-1}$  and one at  $3025 - 3010 \text{ cm}^{-1}$  whereas the  $\text{C}=\text{CH}$  group shows only the lower one of these. They can all vary within  $\pm 10 \text{ cm}^{-1}$ .

Methyl and methylene hydrogens absorb below  $3000 \text{ cm}^{-1}$ . The cyclopropane  $\text{CH}_2$  hydrogens are exceptional. If no methyl bands are detected at  $1385 \text{ cm}^{-1}$  then bands in the  $2800 - 3000 \text{ cm}^{-1}$  region must be due to  $\text{CH}_2$  groups.

The following infra red spectra were taken and are shown in Figs. V to VIII.

#### IR.1

Spectrum of the total reaction products plus cyclopentene. This was not sufficiently different from the spectrum of pure cyclopentene for any deduction to be made.

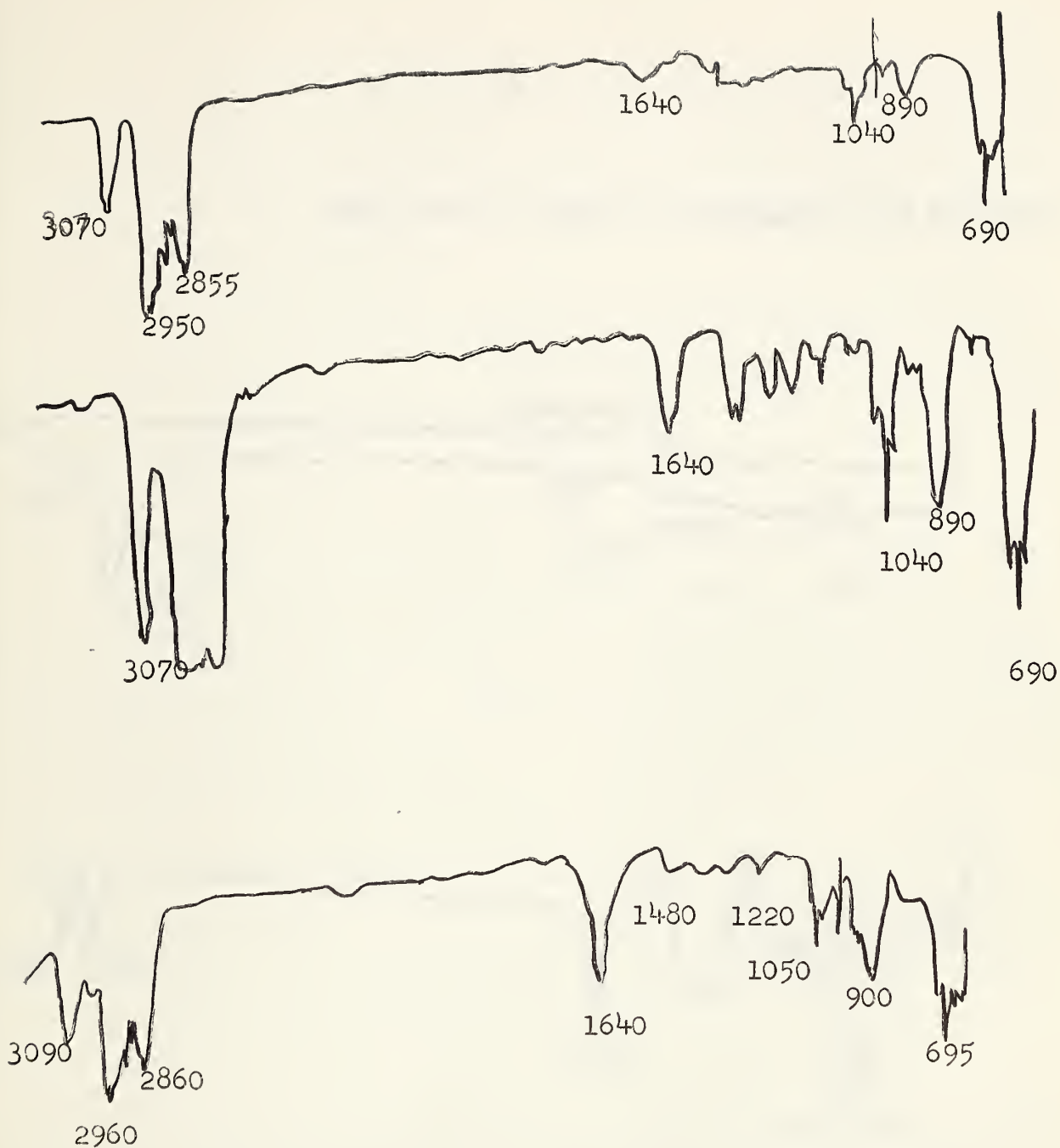
#### IR.2

All the products of several runs were collected as they were eluted from the silica gel column. Some cyclopentene (say 10%) was unavoidably trapped with the products. However significant differences from the spectrum of pure cyclopentene were immediately discerned. The  $1640 \text{ cm}^{-1}$  band was equal in intensity to the bands between  $3000$  and  $2800 \text{ cm}^{-1}$ ; no  $1385 \text{ cm}^{-1}$  band appeared; a shoulder peak appeared at  $3025 \text{ cm}^{-1}$ .









Top: Fig Va  
 Middle: Fig Vb  
 Bottom: Fig VI

Pure cyclopentene - gas phase.  
 Products and substrate - gas phase - IR. 1  
 Products and some substrate - gas phase  
 - IR. 2



Fig. VIII - Total C<sub>10</sub> Products - IR 4 in CCl<sub>4</sub>

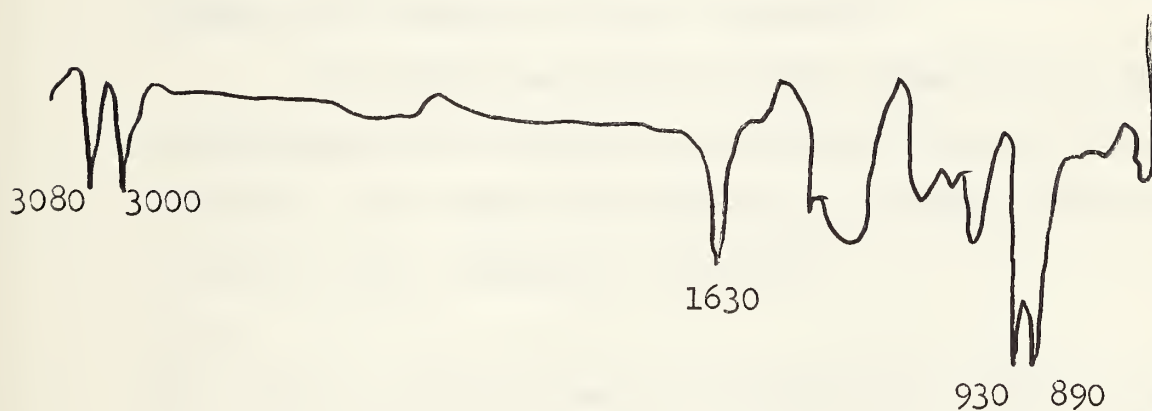
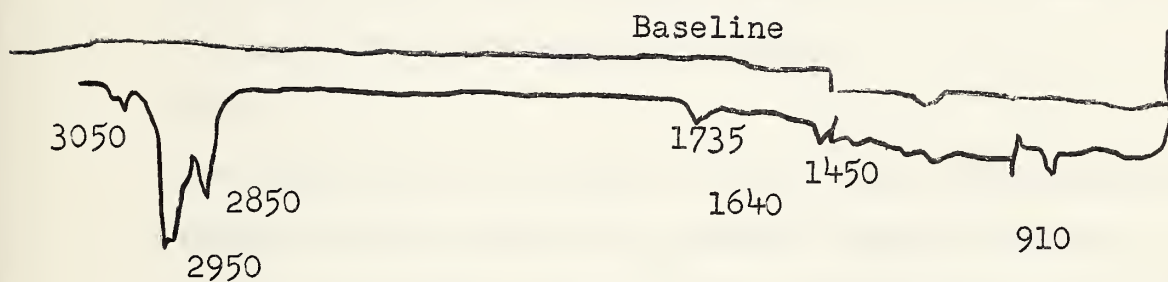


Fig. VII Pure Peak D - IR. 3 in CCl<sub>4</sub>



These observations alone indicate the presence of a terminal olefin group in the products. The rest of this infra red spectrum was not significantly different from that of cyclopentene.

The region below  $1500\text{ cm}^{-1}$  showed that bands at 900, 935, 945, and  $955\text{ cm}^{-1}$  increased in intensity relative to the pure cyclopentene spectrum.

### IR.3

The significant features of this infra red spectrum of highly purified major  $C_5$  product (peak D, figure II) are absence of bands between  $3000 - 2800\text{ cm}^{-1}$  and an intense band at  $1640\text{ cm}^{-1}$ . Comparison of this spectrum with that of vinyl cyclopropane<sup>21</sup> as found in the literature showed them to be identical in all respects.

It should be noted that the presence of vinyl cyclopropane will explain the intense band at  $1640\text{ cm}^{-1}$  in IR.2. The other products ( $C_{10}$ ) probably contributed little to this intensity increase.

### IR.4.

All the  $C_{10}$  products were collected in a trap at the exit from the silica gel column, dissolved in carbon tetrachloride and the infra red spectrum taken. All of these except peak F were shown to be unsaturated by gas



chromatography. Absorption at  $1640\text{ cm}^{-1}$  was very weak and only one weak band appeared above  $3000\text{ cm}^{-1}$  suggesting that the unsaturated  $\text{C}_{10}$  products differ little from cyclopentene.

Tentatively it may be suggested that the  $\text{C}_{10}$  hydrocarbons are bicyclopentyl, cyclopentyl cyclopentene and cyclopentenyl cyclopentene. The spectrum of the cyclopentyl cyclopentenenes has been published<sup>22</sup> and is registered in Appendix I.

#### c) Nuclear Magnetic Resonance Spectroscopy.

All NMR spectra were taken utilizing tetramethyl silane as an internal standard. Any peaks of  $\tau$  value above 9.0 could only be due to methyl protons or those on a cyclopropane ring<sup>23</sup>.

The NMR of the total reaction products including cyclopentene, when compared with that of pure cyclopentene showed extra bands between  $\tau = 9.2$  and  $9.8$ . An infra red spectra of the products showed no methyl groups were present in the products, consequently, the cyclopropane ring must have been present in a product molecule. Confirmation of this was obtained with a solution of the purified  $\text{C}_5$  product which gave an infra red spectrum identical to that of vinyl cyclopropane.





#### d) Mass Spectrometry.

The major  $C_5$  product was trapped separately from both the  $\beta\beta'$  oxydipropionitrile and the silica gel column and re-run twice through the same column to ensure absolute purity before trapping in previously cleaned vessels. The resulting mass spectrum (Appendix II) was found to be independent of the column used for separation. It did not correspond to that of any  $C_5H_8$  molecule registered in the A.P.I. Catalogue. Comparison with the mass spectrum of vinyl cyclopropane is not possible since the latter is not to be found in the literature.

The mass spectrum of the various cyclopentyl cyclopentenes are not known. However the mass spectrum of each  $C_{10}$  product was taken and is shown in Appendix II. The molecular weights of the  $C_{10}$  hydrocarbons in order of elution from silica gel were 138, 136, and 134 corresponding to bicyclopentyl, cyclopentyl cyclopentene and cyclopentenyl cyclopentene.

#### 3. Effect of Exposure Time on Product Formation.

The duration of the runs performed varied from 2.5 to 30 minutes. At a constant cyclopentene pressure of 82 mm vinyl cyclopropane, bicyclopentyl, cyclopentyl cyclopentene, cyclopentenyl cyclopentene and hydrogen were



Table IIA. Product Formation as a Function of Exposure Time.

Pressure = 82 mm. Temperature = 27°C.

Run No.	Duration Runs	u Moles Products					Light Intensity x 10 <sup>6</sup>
		H <sub>2</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>18</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>14</sub>	
* 73	2.5	.20	1.38	.38	1.64	1.38	3.75
* 81	3	.27	-	-	-	-	3.96
* 64	5	.39	2.49	.62	2.39	1.71	2.38
* 72	10	.55	-	-	-	-	2.38
* 78	10	-	5.41	-	5.41	3.89	2.38
* 63	10	.97	7.43	1.25	6.88	4.76	3.75
* 82	10	.75	4.29	1.64	5.30	3.22	2.96
* 74	15	.79	7.59	2.67	7.76	6.11	2.38
* 76	20	1.26	10.0	1.96	9.7	9.1	2.38
* 66	20	1.27	10.8	2.05	8.8	7.1	2.38
* 70	30	1.64	16.0	4.38	14.6	14.9	2.38



Table IIB. Quantum Yield of Products as a Function of Exposure Time.

Cyclopentene Pressure =  $82 \pm 2$  mm.  
 Temperature =  $27 \pm 2^\circ\text{C}$ .

Run No.	Time mins.	Quantum Yield of Products				
		H <sub>2</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>18</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>14</sub>
70	30	.023	.22	.06	.20	.20
76	20	.026	.21	.04	.20	.19
66	20	.026	.22	.05	.20	.15
74	15	.022	.21	.07	.21	.19
82	10	.024	.14	.06	.18	.11
63	10	.026	.20	.06	.18	.13
78	10	.028	.23	-	.20	.17
64	5	.032	.21	.05	.20	.16
81	3	.023	-	-	-	-
68	2.5	.042	-	-	-	-
73	2.5	.021	.15	.04	.18	.15
80	1.5	.030	-	-	-	-



Fig II Quantum Yield of Products as a Function of Exposure Time

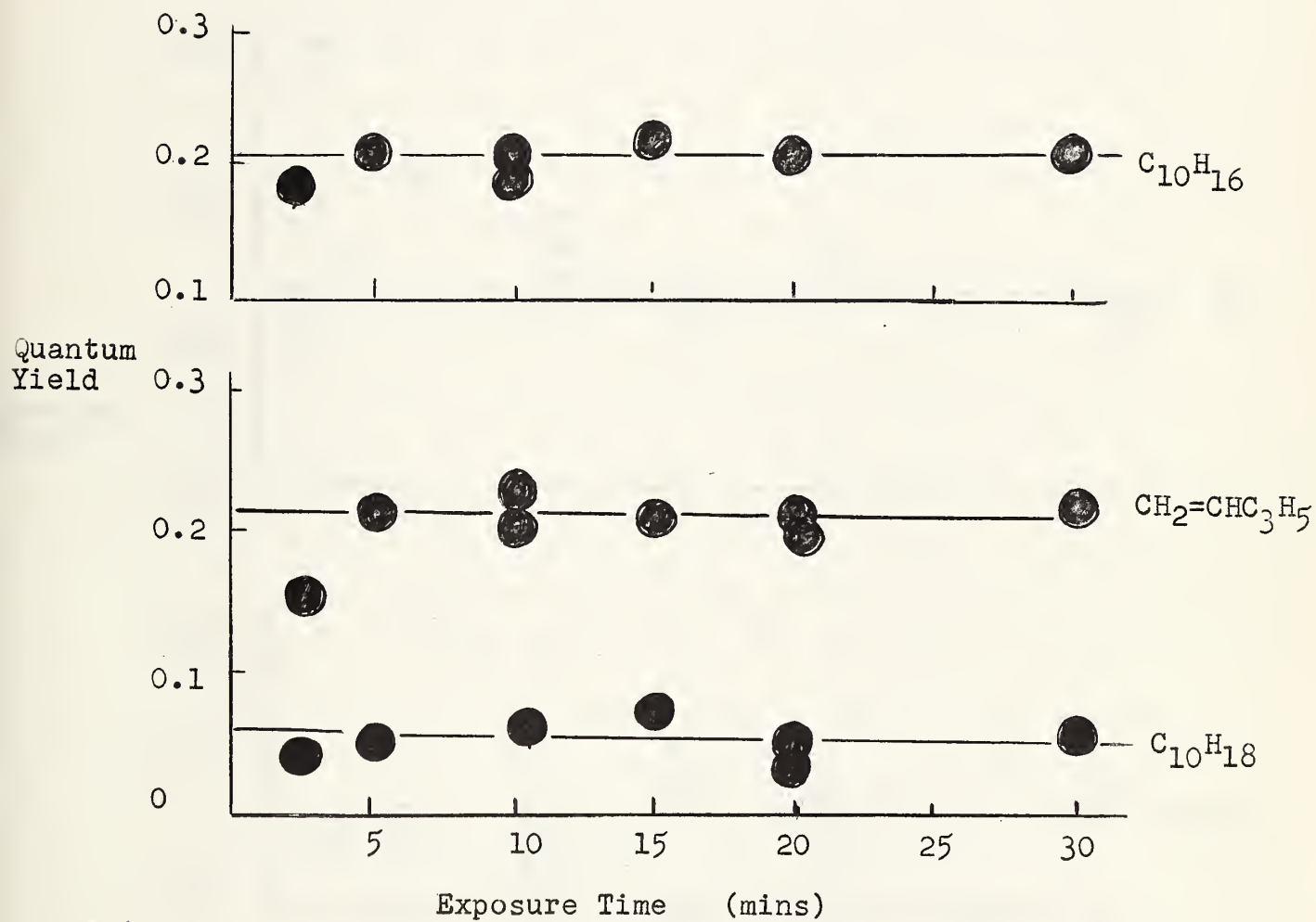
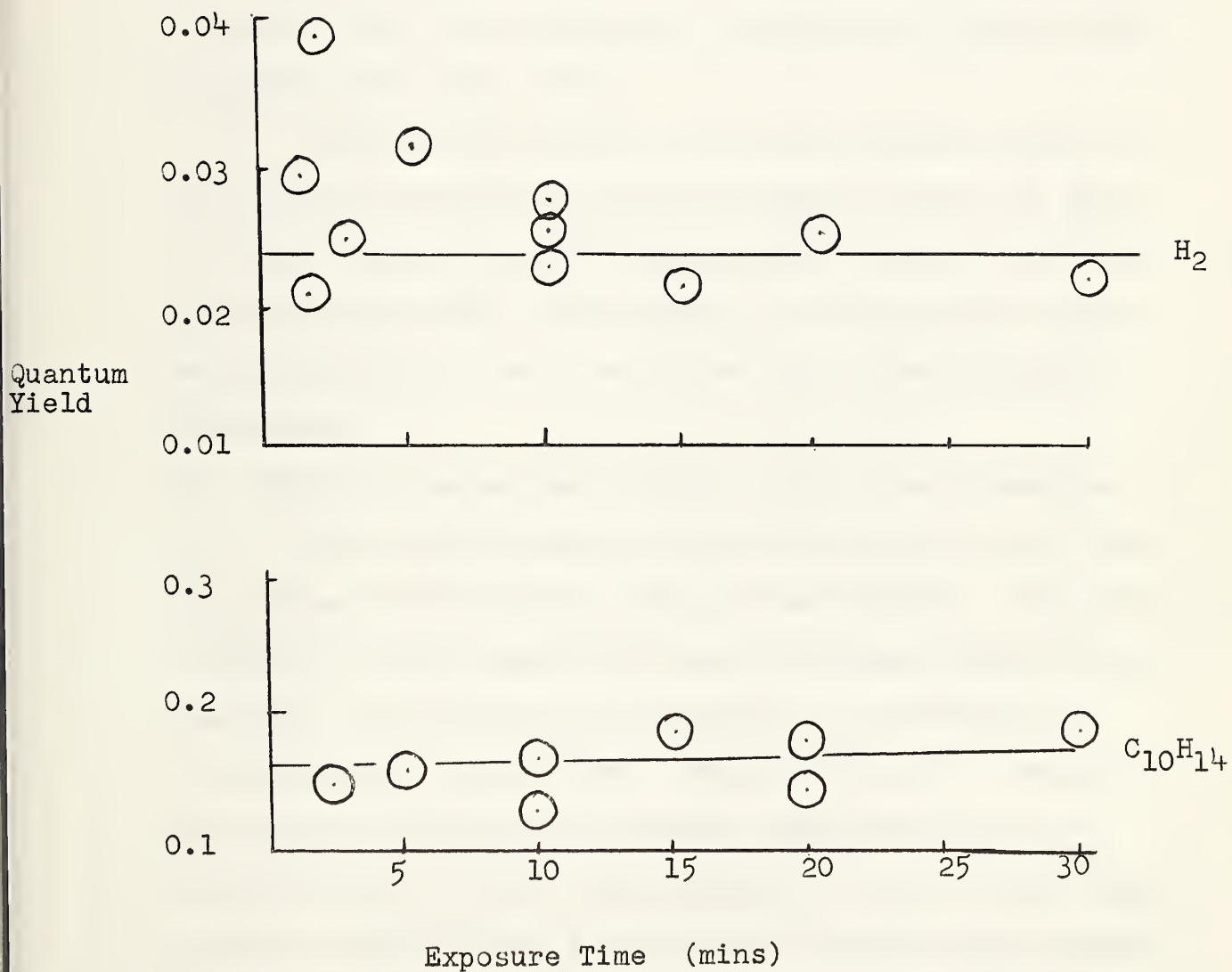






Fig II Quantum Yield of Products  
as a Function of Exposure Time





the only products measured. Although they still remained relatively unimportant products, at higher exposure times, 1:4 pentadiene and cyclopentadiene increased.

The yield of major products in micromoles is shown in Table IIA and the quantum yield of product formation in Table IIB. The latter was plotted as a function of exposure time (Fig. III).

Within experimental error the quantum yield of all products measured was independent of exposure time. At small exposure runs it necessarily follows that the experimental error will increase. To study this range more accurately a more sensitive gas chromatograph is necessary.

#### 4. Effect of substrate pressure of product formation.

The cyclopentene pressure was varied from 20 mm. to 135 mm at an exposure time of ten minutes. The principal products in this range were again hydrogen, vinyl cyclopropane, bicyclopentyl, cyclopentyl cyclopentene and cyclopentenyl cyclopentene. Below 30 mm, the syringe technique for introducing samples made analysis for hydrocarbons a little less accurate. Also in this range visible signs of both a liquid and a white solid polymer appeared and trace  $C_5$  products became more important. A



Table IIIA. Product Formation as a Function of Cyclopentene Pressure.

Exposure Time = 10 minutes.

Temperature = 27°C.

Run No.	Pressure mm Hg	Quantum Yield Products					Light Intensity $\times 10^6$
		H <sub>2</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>18</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>14</sub>	
114	5.4	1.71					3.94
113	5.4	2.17					2.96
112	11	1.32					3.94
111	11	1.86					2.96
108	20	1.16	8.2	1.43	8.0	7.1	2.96
107	20	1.53	11.3	1.64	9.0	7.9	3.94
60	26	0.92	8.0	0.68	3.48	3.3	2.38
* 77	30	1.13	8.8	-	-	-	3.75
98	30	-	8.1	1.19	6.45	5.6	2.96
* 75	30	1.26	8.0	2.00	8.00	5.7	3.75
61	33	1.37	-	-	-	-	3.75
59	39.4	1.16	10.1	1.45	7.30	6.3	3.75
53	46		9.7	1.72	6.66	6.1	3.75
* 69	52	-	10.8	1.28	6.54	5.2	3.75
57	67.5	1.0	7.5	0.57	6.0	5.4	3.75
* 63	82.5	0.97	7.4	1.25	6.0	4.8	3.75
47	106	1.0	6.6	1.17	4.97	3.5	3.75
45	124	0.94	5.6	1.69	5.4	4.7	3.55
* 65	135	0.87	5.9	1.70	6.18	5.3	3.75
43	135	1.0	6.8	1.24	3.57	3.6	3.55



Table IIIB. Quantum Yield of Product Formation as a Function of Cyclopentene Pressure.

Exposure Time = 10 minutes  
Temperature = 27°C.

% Decomposition of Cyclopentene = 18% (20 mm) to 1.4% at 135 mm.

Run No.	Pressure mm Hg	Quantum Yield of Products				
		H <sub>2</sub>	C <sub>5</sub> H <sub>8</sub>	C <sub>10</sub> H <sub>18</sub>	C <sub>10</sub> H <sub>16</sub>	C <sub>10</sub> H <sub>14</sub>
114	5.4	.055				
113	5.4	.058				
112	11	.044				
111	11	.047				
108	20	.040	.30			
107	20	.038	.29	.042		
60	26	.039		.029		
77	30	.030	.24	-	-	-
98	30	.034	.28	.040	.22	.19
75	30	.034	.24	.053	.22	.16
61	33	.036	-	-	-	-
59	39	.031	.26	-	.19	.16
53	46	.031	.24	.043	.17	.16
69	52	-		.034	.17	.14
57	68	.027	.20	.03	.16	.14
63	83	.026	.20	.042	.18	.13
47	106	.029	.19	.033	.14	.10
45	124	.027	.18	.048	.15	.13
65	135	.023	.16	.045	.16	.14
43	135	.029	.21	.030	.14	.14





Fig III Quantum Yield of Products as a Function of Cyclopentene Pressure

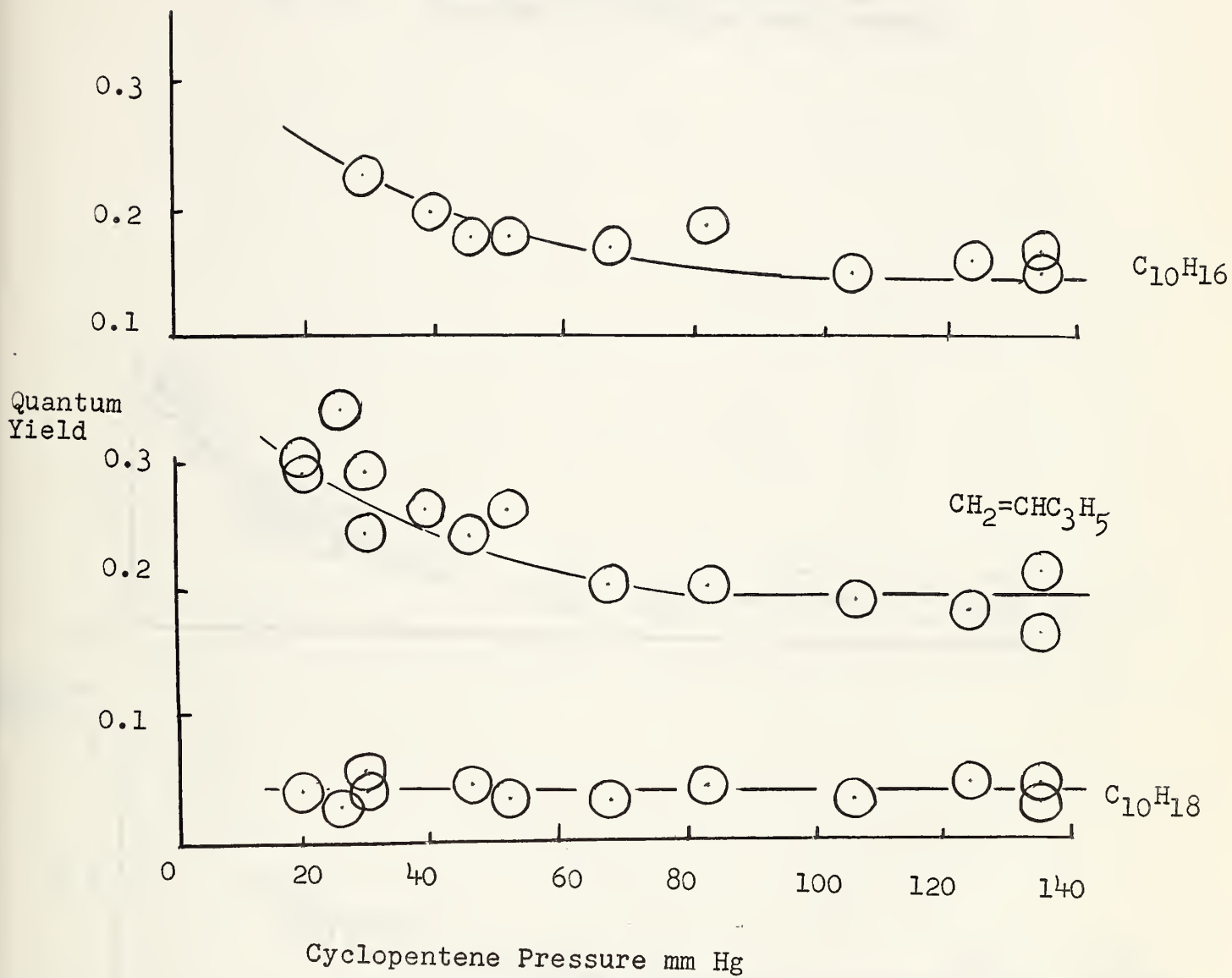
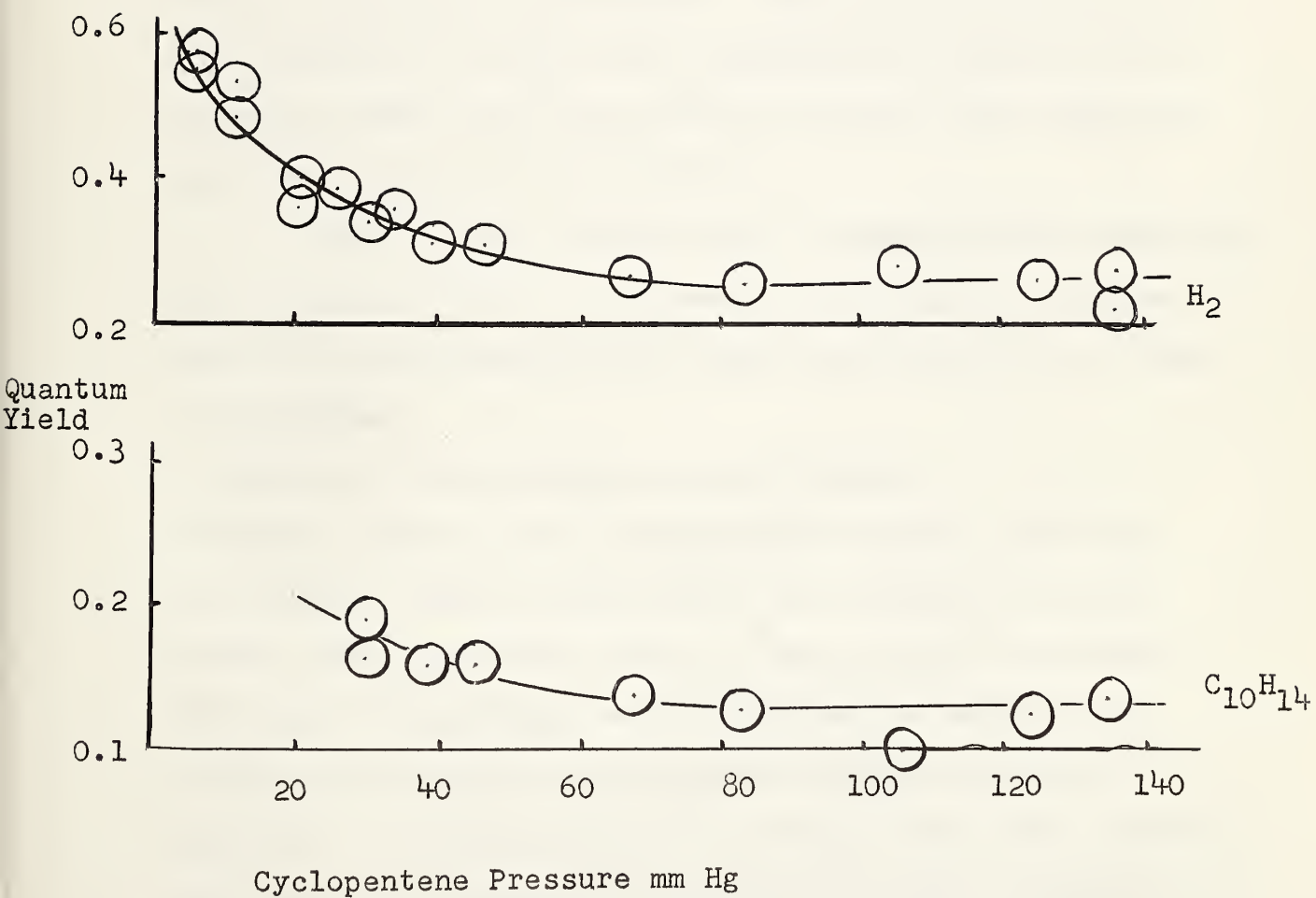




Fig III Quantum Yield of Products as a Function of Cyclopentene Pressure





small immeasurable amount of another hydrocarbon, probably a  $C_{10}$  compound, showed up after cyclopentenyl cyclopentene.

The variation in major products with pressure is depicted in Tables IIIA and IIIB and a graph of quantum yield of products against cyclopentene pressure is shown (Fig. II).

A pressure effect on all products except bicyclopentyl is clearly discernible. This latter product has a quantum yield of only 0.04, consequently detection of a pressure effect would be difficult unless more sensitive apparatus was used for analysis.

Cyclopentane did not have a quantum yield exceeding 0.01 to 0.02. Even at a pressure of 10 mm, the quantum yield of cyclopentadiene was only one tenth that of vinyl cyclopropane.

#### 5. Effect of Added Gases on the Products.

a) Nitric Oxide: At a cyclopentene pressure of 40 mm and exposure time of ten minutes the pressure of added nitric oxide was varied from 2.5 mm to 25 mm. Hydrogen and vinyl cyclopropane were unaffected by addition of nitric oxide, but all the  $C_{10}$  hydrocarbon products disappeared. A yellow product was formed which was separated from the other products, dissolved in carbon tetrachloride



and its infra red spectrum taken. Two distinct bands around  $3600\text{ cm}^{-1}$  showed it to be an oxime.

b) Inert Gases: At a cyclopentene pressure of 30 mm the products decreased very slightly on the addition of sulphur hexafluoride and krypton to a limit of 100 mm and 300 mm respectively. However, later work, extending the pressure range of cyclopentene below 30 mm indicated that a more discernible pressure effect might have been found by working at 10 mm of cyclopentene.





#### IV Discussion

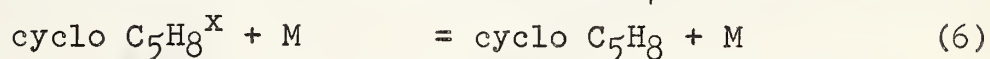
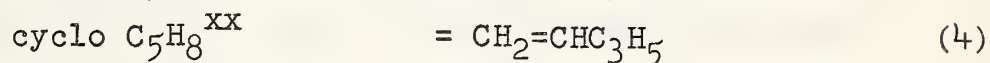
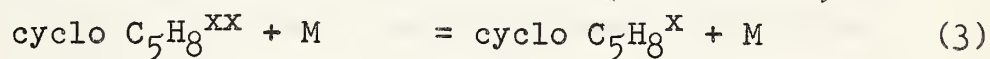
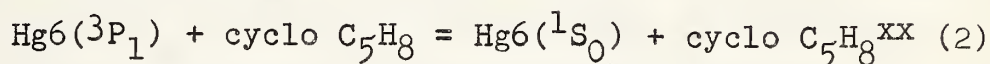
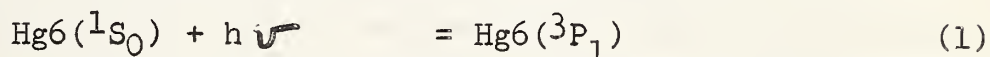
Any mechanism which is proposed will have to fit the following observations.

1. The major products are vinyl cyclopropane, cyclopentyl cyclopentene, cyclopentenyl cyclopentene, bicyclopentyl and hydrogen. Cyclopentane becomes a product of any significance only at lower pressures. At 20 mm cyclopentene the quantum yield of cyclopentane does not exceed 0.02.
2. Compared with the quantum yield of condensible products, that of hydrogen is low.
3. The quantum yield of all products is independent of exposure time.
4. Addition of nitric oxide reduces the quantum yield of the C<sub>10</sub> products to zero but does not appreciably affect the yield of hydrogen and vinyl cyclopropane.
5. The quantum yields of all products except bicyclopentyl exhibit pressure dependence. Further more, the effect of increasing the pressure of cyclopentene affects all products in a similar manner.
6. A steady state is reached beyond the region of 50-60 mm cyclopentene. Inert gases, when added in appreciable amounts, even at moderately high pressures, do not lower the quantum yield of products below the steady state value.



7. Polymer is formed, particularly at low pressures and long exposure times.

The following mechanism is the one which best fits the experimental results. It will later be shown that it also fits into the general pattern for olefin decompositions described in the introduction.



From the affect of pressure on the reaction products it can be seen that the initial step in the decomposition of cyclopentene is the same as that postulated for other olefin decompositions viz interaction between the  $\pi$  electrons of the double bond and the metal atom to form a vibrationally excited triplet state molecule,  $\text{cyclo C}_5\text{H}_8^{\text{xx}}$ . The vibrational energy can be removed in steps by any gas M (step 3) to form, eventually, a ground triplet state molecule,  $\text{cyclo C}_5\text{H}_8^{\text{x}}$ . The transition from a higher to the lowest vibrational level of triplet state is a rapid one but may require several collisions. Reactions (4) and (5) can be assumed to occur less readily the lower the amount of vibrational excitation in the molecule. Because of spin conservation the lifetime of this ground triplet state will be long.



The question arises of whether all the products come from a single excited state or from two different excited states.

The formation of vinyl cyclopropane must involve breakage of the  $\beta$  C-C bond with formation of the C-C bond of the cyclopropane ring. Whether this occurs via an intermediate biradical which is at the same time an allyl type radical, or else, by direct isomerization in which one bond breaks while the other is being formed (as shown) is a question which the experimental evidence cannot fully answer.



However, the action of nitric oxide on the products gives some insight into the problem. Vinyl cyclopropane and hydrogen were unaffected but the  $C_{10}$  hydrocarbons were eliminated from the products. As will be shown later, the  $C_{10}$  hydrocarbons are formed by radical reactions. Thus nitric oxide can be regarded purely as a radical scavenger. The work of Thrush and Clyne<sup>24</sup> has shown why the quantum yield of hydrogen is not affected. Two explanations are available for the formation of vinyl cyclopropane. Either it is a direct isomerization or the biradical formed cyclizes so rapidly that it cannot be scavenged by nitric oxide.

Flowers and Frey<sup>25</sup> have studied the thermal isomerization of vinyl cyclopropane. In the temperature





range 339 - 390° the reaction is truly unimolecular. The pre-exponential factor of  $10^{13.5} \text{ sec}^{-1}$  puts it in the group of unimolecular reactions in which little change in entropy occurs in going to the transition state. The activation energy is relatively low - 49.6 kcal. These observations indicate the reaction involves a direct isomerization of vinyl cyclopropane to cyclopentene and suggests that the vinyl cyclopropane is formed in this study also by direct isomerization (step 3). It now remains to be shown that both vinyl cyclopropane and the  $C_{10}$  products probably arise from the vibrationally excited rather than the ground state triplet cyclopentene molecule.

An examination of Fig. III shows that the effect of pressure on all products is qualitatively the same. This implies they all have similar precursors, and that these precursors becomes less and less capable of giving rise to products as the pressure of substrate increases, eventually reaching a steady state around 50 - 60 mm. An explanation can be found, if the precursors have vibrational energy which can be removed more efficiently at higher pressures. However, it is not impossible that the ground triplet state can give rise to these products and the vibrationally excited states do so more readily<sup>30</sup>.

kcal.

—— 112  
cyclo  $C_5H_8^{xx}$

—— 77  
cyclo  $C_5H_7 + H$

↑ 50  
↓  
cyclo  $C_5H_8^x$   
↓  
20

—— T.S.  
Frey 50  
and  
Flowers

——  
cyclo  $C_5H_8$

——  
 $CH_2=CHC_3H_5$



Consideration of the energetics of the reactions and excited states involved should shed some light on this problem. Certain assumptions are necessary viz

(a) the ground state of vinyl cyclopropane has the same or greater energy than that of cyclopentene (from thermochemical data).

(b) the energy of the first vibrationless triplet state of cyclopentene lies in the 20 - 50 kcal region<sup>12</sup>.

(c) the transition state (T.S. in diagram) for the cyclopentene isomerization to vinyl cyclopropane is the same as that for the reverse thermal isomerization.

(d) Allyl hydrogen bond dissociation energy in cyclopentene is 75 - 80 kcal.

Inspection of the diagram opposite shown that it is not impossible to form vinyl cyclopropane from the ground triplet state molecule  $C_5H_8^X$ , since this latter molecule can be identical (energetically) with the transition state postulated by Flowers and Frey<sup>25</sup>. On the other hand, 75 kcal is the minimum amount of energy that can break the allyl hydrogen bond (and hence give rise to the  $C_{10}$  fraction). Thus only a vibrationally excited triplet state molecule can give rise to these products. Furthermore, the energy diagram implies that, after a few collisions, not every vibrationally excited molecule will have this energy.



Consequently from the above considerations, the data of Flowers and Frey, and the effect of pressure on the quantum yield of products, it must be concluded that all major products in the mercury photosensitized decomposition of cyclopentene originate from some vibrationally excited triplet state of the cyclopentene molecule.

An alternative mode of formation of vinyl cyclopropane is one similar to that proposed by Robb<sup>14</sup> to account for the extensive rearrangement occurring in the photosensitized decomposition of 2-methyl butene-1. He explained his results by hydrogen atom addition to the substrate giving a hot t-amyl radical which rearranged before losing the hydrogen atom. The appearance of considerable amounts of isopentane in the products was taken as evidence for this mechanism. If Robb's mechanism is to hold true for vinyl cyclopropane formation then by analogy, cyclopentane should be formed in fair yield. This is not the case.

A better explanation of the appearance of the various methyl butenes from 2-methyl butene-1 might be found in direct isomerization from a vibrationally excited triplet state. Rearrangement of the t-amyl radical seems rather unlikely on energetic grounds, although not much is known about the reactions of hot radicals. One other

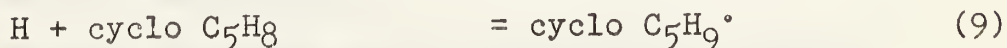


argument Robb uses to favour his mechanism is that the rearrangement of the di-tert-butyl-carbinyl-radical (a secondary radical) to the corresponding tertiary radical readily takes place. However, t-amyl may be different--it can only form a secondary or primary radical by rearrangement, both of which are less stable than itself.

In any case, the apparent high extent of reaction in Robb's experiments leaves room for uncertainty. Perhaps some of his products arise by secondary reactions.

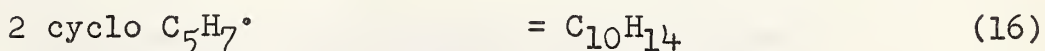
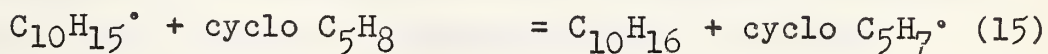
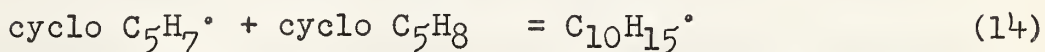
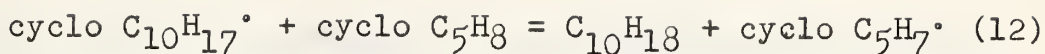
It is proposed the  $C_{10}$  products originate from the vibrationally excited triplet state of cyclopentene by step (5). A  $\beta$  C-H split thus gives hydrogen atoms and cyclopentenyl radicals. The hydrogen atoms then add to the substrate giving cyclopentyl radicals.

The occurrence of  $C_{10}H_{18}$ ,  $C_{10}H_{16}$  and  $C_{10}H_{14}$  in the products could be accounted for by simple recombination reactions but the ratio of the  $C_{10}$ 's, the appearance of polymer, the absence of cyclopentane and low quantum yield of hydrogen are not explicable solely on this basis. A mechanism that would explain these factors is shown:









Stock<sup>19</sup> showed that cyclopentyl radicals should recombine and disproportionate with equal efficiency. The reactions of allyl radicals, particularly at room temperature, have not been studied in any detail. At high temperatures Bryce and Ruzicka<sup>26,27</sup> found that abstraction and addition reactions occur readily. In their system, disproportionation and combination would not be apparent. At room temperature, addition reactions should predominate over abstraction<sup>29</sup>. Kebarle<sup>28</sup> generated allyl radicals at room temperature and studied their recombination reactions. They were found to recombine as readily as methyl radicals.

The above mechanism contains some element of speculation since absolute identification of the  $C_{10}$  hydrocarbons was not obtained and the reactions of allylic radicals are not well known.

Polymer formation can be explained by further addition of  $C_{10}$  radicals to cyclopentene and so on. A





clue to the relative importance of recombination and addition reactions of the  $C_5$  radicals can be found from the results. If bicyclopentyl is formed solely by recombination (reaction 17) then an equal amount of cyclopentane must be formed--Stock<sup>19</sup>. Consequently bicyclopentyl must be formed principally by a method other than combination of cyclopentyl radicals, viz reactions (11) and (12), postulating addition of the cyclopentyl radical to cyclopentene followed by abstraction by the  $C_{10}H_{17}$  radical. However, if the  $C_{10}H_{17}$  radical can abstract hydrogen, the  $C_5H_9$  should also abstract. Since little cyclopentane was found it may be assumed that the bulkiness of the  $C_{10}H_{17}$  radical makes abstraction relatively more important.

Cyclopentadiene, like cyclopentane, has a maximum quantum yield of 0.02. It should form by disproportionation of cyclopentenyl radicals. McColl and Thomas<sup>31</sup> found that cyclopentadiene is about twice as efficient as cyclohexene in inhibiting chain reactions. Consequently, disproportionation of cyclopentenyl radicals must also be relatively unimportant compared with their addition and abstraction reactions. These latter reactions cannot be detected in this system. Thus, the formation of  $C_{10}H_{16}$  and  $C_{10}H_{14}$  are shown in the mechanism to form in a manner analagous to that proposed for bicyclopentyl formation--reactions



(13), (14), (15), and (16).  $C_{10}H_{14}$  is probably formed only by reaction (14), thus recombination of cyclopentenyl radicals would seem more important than disproportionation.

#### Conclusion.

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The mechanism proposed for the decomposition of cyclopentene is consistent with the experimental observations. All products arise from excited vibrational levels of a triplet state of cyclopentene. Vinyl cyclopropane appears to be formed by direct isomerization. The  $C_{10}$  hydrocarbons originate from the fragments formed by scission of the allylic hydrogen bond. Reactions of the cyclopentyl and cyclopentenyl radicals give rise to  $C_{10}$  products both by intercombination and addition followed by abstraction reactions. The low quantum yields cyclopentane and cyclopentadiene imply that disproportionation can only be occurring to a minor extent. Also the larger quantum yield of  $C_{10}H_{14}$  formation implies that the combination is at least a factor of ten times as fast as disproportionation.

Within experimental accuracy the quantum yields of products are independent of exposure time over the range 2.5 to 30 minutes. All products decrease in a similar manner to a steady state with increasing substrate pressure. No explanation of this phenomenon has been proposed.



The mechanism proposed fits the general pattern for olefin decompositions laid down in the introduction. It differs in that it postulates no products can arise from the ground triplet state. It was previously postulated that cis-trans isomerization occurred from this latter state but this reaction cannot occur with cyclopentene. The possibility that vinyl cyclopropane arises from the ground vibrational level could be checked by observing the decomposition of cyclopentene photosensitized by molecules such as sulphur dioxide and biacetyl.



## V Bibliography

1. E.W.R. Steacie "Atomic and Free Radical Reactions" Reinhold, 1954, 2nd edition.
2. R.A. Back, Can. J. Chem., 71, 1834 (1959)
3. S. Bywater and E.W.R. Steacie, J. Chem. Phys., 19 319 (1951).
4. B.A. Callear and R.J. Cvetanovic, J. Chem. Phys., 24, 873 (1956).
5. B.A. Callear and R.J. Cvetanovic, ibid, 23, 1182 (1956)
6. F.P. Lossing, D.G.H. Marsden and J.B. Farmer, Can. J. Chem., 34, 701 (1956).
7. D.J. Leroy and E.W.R. Steacie, J. Chem. Phys., 2, 829, (1941).
8. G. Porter, Discussions Faraday Soc., 17, 94 (1954).
9. H.E. Gunning and E.W.R. Steacie, J. Chem. Phys., 14, 581, 1946.
10. R.B. Cundall and T.F. Palmer, Trans. Far. Soc., 56, 1210, 1960.
11. H.E. Gunning, R.J. Cvetanovic and E.W.R. Steacie, J. Chem. Phys., 31, 573 (1959).
12. C. Reid, Quart. Revs., 12, 205 (1958).
13. M. Avrahami and P. Kebarle, "Informal Conference on Photochemistry - Abstracts", Univ. of Alberta, 1961.
14. J.R. Majer, B. Mile and J.C. Robb, Trans. Far. Soc., 57, 1336, 1961.
15. K. Laidler, "Chemical Kinetics of Excited States", Oxford Univ. Press, 1955.
17. C. Reid, Quart. Revs., 1958.
18. B. Bellamy, "The Infra Red Spectra of Complex Molecules", Methuen, 1957.







19. R.L. Stock, Ph.D. Thesis, Univ. of Alberta, 1961.
20. G.D. Lutwick, Ph.D. Thesis, Univ. of Alberta, 1961.
21. Van Volkenburgh, Greenlee, Derfer and Boord, J. Am. Chem. Soc., 71, 3549 (1949).
22. C.F. Blakely, R.J. Gillespie, L. Roubinek, A. Wasserman, and R.F.M. White, J. Chem. Soc., 1939 (1961).
23. L.M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy to Organic Chemistry", Pergamon Press, 1959.
24. B.A. Thrush and M.A.A. Clyne, Trans. Far. Soc., 57, 1305, (1961).
25. M.C. Flowers and H.M. Frey, J. Chem. Soc., 3547, 1961.
26. D.J. Ruzicka and W.A. Bryce, Can. J. Chem., 38, 827 (1960).
27. D.J. Ruzicka and W.A. Bryce, Can. J. Chem., 38, 835 (1960).
28. P. Kebarle, Paper Presented at the Conference on Mass Spectrometry, University of Oxford, 1961.
29. N.N. Semenov, "Some Problems in Chemical Kinetics" Vol I, Princeton University Press, 1958.
30. G.B. Porter and R.M. Hochstrasser, Quart. Revs., 2, 1960.
31. A. Maccoll and P.J. Thomas, J. Chem. Soc., 5033 (1957).



## Appendix I

### Infra Red Absorption Spectra

Key: I: Mixed cyclopentylcyclopentenenes  
II: Bicyclopentyl

I	II
3049	2944s
2941s	2857s
2865s	1471
1634	1447s
1600	1359
1437s	1326
1335	1299
1312	1250
1285	1026
1200	963
1157	926
1031	893
943	
926	
900	
893	
800	
719s	



## Appendix II

### Mass Spectra of Products

Mass No.	I	II	III	IV
27	29.1	31.1	6.31	11.5
29				7.2
38	12.8		5.0	9.9
39	70.7	73.7	23.9	45.8
40	33.8	31.8	19.0	29.8
41	37.2	38.8	1.32	22.9
42	19.7	20.8	3.02	6.5
51	6.86	7.09		
53	59.4	59.4	8.24	16.
65	17.6	16.2	15.4	28.0
66	6.75	6.85	30.2	55.4
67	100	100	100	100
68	52.4	56.2	19.5	28.2
69			3.5	3.8
77			1.29	2.3
78			.4	
79			2.07	3.1
81			9.6	
91			1.30	2.3
95			3.89	
105			.23	
107			.46	
134				1.4
135				
136			2.85	
137			.23	

I: Peak D trapped from  $\beta\beta'$ -oxydipropionitrile.

II: Peak D trapped from silica gel.

III: Peak C+ trapped from silica gel.

IV: Peak H trapped from silica gel.

V: A reproducible mass spectrum of bicyclopentyl was not obtained.



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